# mcPSI: A Monte Carlo phase space integral code for calculating accurate anharmonic vibrational properties of molecular systems

## Background

Vibrational anharmonicity is often neglected in practical rate calculations of molecular systems. This ubiquitous (harmonic) approximation can result in significant errors, particularly at the high temperatures and energies relevant to combustion.

## New theory

- Here we present an accurate and generally applicable approach for calculating vibrationally anharmonic molecular properties using classical Monte Carlo integration of phase space. The new method employs numerical evaluations of the Jacobian, allowing for the use of "chemist's coordinates" (stretches, bends, and torsions).
- Efficiency improvements are realized via decompositions of the full-dimensional vibrational state density into "intrinsic" pairwise, 3-mode, etc., state densities.

## Code

- A stand-alone code that produces corrections to harmonic properties for use as inputs to the AITSTME code
- "Embarrassingly" parallel, e.g., direct (QCISD(T)/CBS) `mcPSI` calculations for vinyl took 14 h on ~1000 cores
- Availability: Coming soon


E. Kamarchik and A. W. Jasper, J. Chem. Phys. **138**, 194109 (2013).
E. Kamarchik and A. W. Jasper, J. Phys. Chem. Lett., submitted (2013).


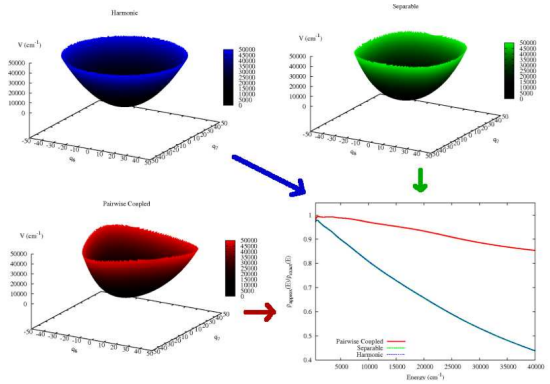


Fig 1. The potential energy surface associated with two modes of methane in the harmonic approximation (blue), the uncoupled anharmonic approximation (green), and without approxiamtion (red). We have demonstrated that the full-dimensional anharmonicity of methane can be recovered via evaluations of only the pairwise potentials.

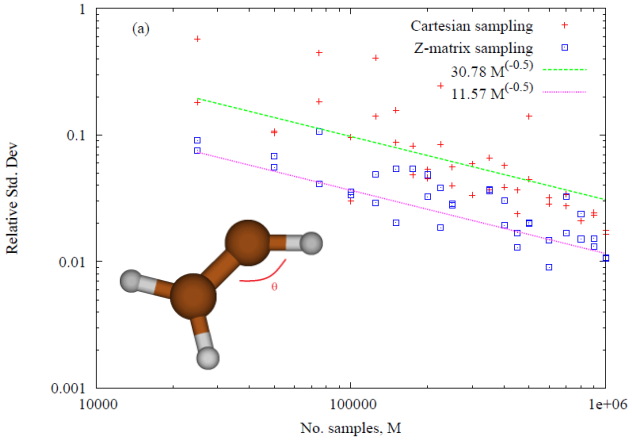


Fig 2. A demonstration of the 10x improvement in efficiency obtained using stretch/bend/torsion coordinates relative to the more commonly used Cartesian normal mode coordinates.